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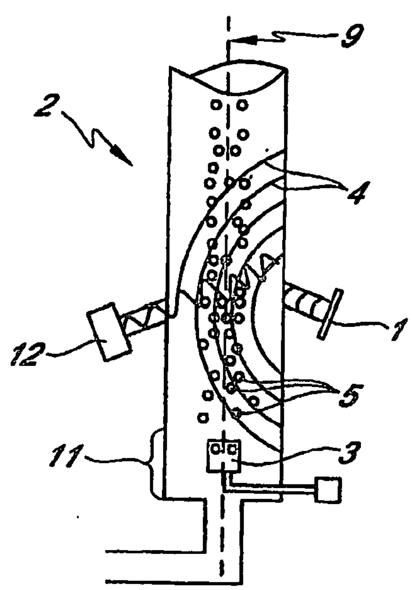
Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv)) for US only*

[Continued on next page]

(54) Title: DEVICES AND PROCESSES FOR USE IN ULTRASOUND TREATMENT



(57) **Abstract:** Devices and methods for treating, preventing from growth, and neutralizing microorganisms from a cutting or a fountain solution using high-frequency, low-energy ultrasound (4) in combination with gas microbubbles (5).

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construed broadly, and generally relates to an apparatus containing fountain solution. In specific embodiments the devices provided herein are connected (*e.g.*, via a side stream) to a fountain solution distribution, supplying, collecting, mixing, or circulating system. In further embodiments, the devices provided herein are not in communication with a reservoir, but are directly connected to the fountain solution to be treated.

[0064] In other embodiments, the compartment 2 contains (*e.g.*, along its wall) one or more high-frequency ultrasound emitters 1 that emit ultrasound 4 into the compartment 2, preferably into the center of the compartment 2. In other embodiments, the container can also have one or more gas microbubble emitters 3 for emitting gas microbubbles 5, which are arranged so as to emit the gas microbubbles 5 into the ultrasound 4 field emitted in the compartment 2.

[0065] The term "microbubbles," as used herein is intended to refer to gas bubbles with an average diameter of less than 1 mm. In some embodiments, the diameter is less than or equal to 50 μm. Still in other embodiments, the microbubbles have a diameter less than about 30 μm. In certain embodiments, the microbubbles are selected from air, oxygen, and ozone microbubbles. To lower operating costs, it can be advantageous to use microbubbles that are not ozone microbubbles, such as air microbubbles.

[0066] The term "microorganism," is synonymous with "microbe", and generally relates to any pathogenic or non-pathogenic microorganism which can give rise to harmful effects to the printing system (*e.g.*, fountain solution, printing plates, machines, instruments), man, mammals or any other animal. Such microorganisms can include both aerobic and anaerobic bacteria (*e.g.*, *Yersenia*, *Staphylococcus, E. coli, Pseudomonas aeruginosa, Pseudomonas oleovorans, Paracolobactrum, Proteus vulgaris, Klebsiella pneumoniae, Micrococcus pyogenes, Aerobacter aerogenes, Citrobacter, Achromobacter*), viruses (*e.g.*, HIV, HCV, HBV), fungi (e.g. *Fusarium*, *Cephalosporium*, *Cladosporium*, *Aspergillus*), protists (*e.g.*, mold), and the like.

[0067] In specific embodiments, the methods and devices herein include low energy, high-frequency ultrasound to treat a fountain solution. The term "high frequency" is intended to refer to frequencies higher than 200 kHz and up to several MHz. In certain embodiments, the high frequencies used are between 200 kHz and 10 MHz. In still other aspects, the high-frequencies can be between 200 kHz and 20MHz. In various other embodiments, the high-frequencies can be between 800 kHz (where less radical effects and more biological effects are reached) and 5MHz. In another embodiment, the frequency

used is between 1 MHz and 3 MHz. More specifically, the frequency can be about 1.8 MHz.

[0068] In various embodiments of the methods and devices described herein, the gas microbubble emitter 3 for emitting gas microbubbles 5 is arranged at the base 11 of the compartment 2, (*i.e.*, at the bottom of the compartment 2), such that the microbubbles move by rising naturally or by entrainment of the gas in the flow of the fountain solution.

[0069] In still further embodiments, the devices and methods described herein can neutralize, treat or prevent the growth of microorganisms in a fountain solution. Although the present teachings are in no way to be limited by their precise mechanism of action, in more specific embodiments the devices provided herein can produce radicals such as $ROO^{\cdot}$, $H^{\cdot}$, $^{\cdot}OH$ and $HOO^{\cdot}$ which can also form H_2O_2. This molecule and/or these radicals being toxic to microorganisms and thus bring about their inactivation and/or destruction.

[0070] The species created are thought to be derived from the reactions of high-frequency ultrasound on the water molecule, most likely giving rise (in particular in the presence of oxygen) to the following reactions:

$H_2O \rightarrow H^{\cdot} + {}^{\cdot}OH$

$H^{\cdot} + O_2 \rightarrow HOO^{\cdot}$

$HOO^{\cdot} + HOO^{\cdot} \rightarrow H_2O_2 + O_2,$

${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$

[0071] Advantageously, the energy utilized to produce these toxic species is reduced if the process if performed in the presence of microbubbles, as described herein.

[0072] It has been recently appreciated that the injection of microbubbles into the ultrasound field gives rise to an increase in the phenomenon of sonoluminescence, by superposition of the microbubbles onto the cavitation bubbles induced by the ultrasound, the number of excited and toxic species can be multiplied. This phenomenon is observed on a macroscopic level when the ultrasound treatment is synergistically combined with the presence of microbubbles of suitable size.

[0073] In additional embodiments, the devices and methods provided herein have the advantage that there is no need to devote the ultrasound to specific zones, since it is observed that the treatment system functions by diffusing the products formed *in situ*

(*e.g.*, ROS (reactive oxygen species), radicals and H_2O_2) towards the reservoir of fountain solution to be treated.

[0074] In further embodiments, the one or more ultrasound emitters 1 in the devices described herein are oriented so as not to give rise to any standing-wave phenomena. For example, in certain embodiments, one or more ultrasound emitters can be oriented obliquely relative to the axis 9 of the compartment 2 (acute angle not perpendicular to this axis 9) and relative to the flow of fountain solution and to the flow of microbubbles 5 (see Figure 1). This characteristic makes it possible for practically all the microbubbles 5 in the compartment 2 to be treated in a statistically identical manner, without creating stationary zones in the said compartment 2. Accordingly, certain embodiments herein are directed to devices and methods that provide substantially uniform treatment and protection over time.

[0075] According to other embodiments, the devices and methods described herein can include a light emitter 12 (*i.e.* an electromagnetic radiation emitter) which emits into the compartment 2 in the ultrasound 4 field, radiation, with a frequency that is mostly in the visible range. However, for certain applications, in order to remove certain specific microorganisms, it can be advantageous to emit electromagnetic radiation with a frequency that is mostly non-visible, as ultraviolet radiation (*e.g.*, UVA, UVB or UVC type), infrared, laser, microwaves, and the like, for example.

[0076] It has recently been discovered, unexpectedly, that a treatment comprising the emission of microbubbles into a field, combined with ultrasound and light radiation is particularly effective at inactivating and removing microorganisms present in a fountain solution. The phenomenon of sonoluminescence can promote the production of extremely active oxygenated species (often referenced as ROS: reactive oxygen species) such as the superoxide radical, $^{\cdot}OH$, or singlet oxygen, which can result in a series of biochemical reactions that are extremely toxic for certain microorganisms.

[0077] In various embodiments, the teachings herein are directed towards devices which do not require additional chemical products (*e.g.*, biocides, photosensitizers) to neutralize or prevent the growth of microorganisms, from a fountain solution. In other embodiments, the devices herein can be used to neutralize, or prevent the growth of microorganisms in a fountain solution, with a limited amount of chemical products (*e.g.*, biocides, photosensitizers). The term "limited amount" relates to solutions containing less than 5 ppm of biocide. For example, a limited amount of biocide can include about 4.9,

4.5, 4.0, 3.0, 2.0, 1.0, and 0 ppm, and any value or range of values between these values. The term "biocide" is to be construed broadly, and generally relates to any suitable agent that is capable of preventing or stopping the growth of microorganisms, including bacteria, mold, algae, fungus, viruses, protists, and the like, for example.

[0078] In other embodiments, the devices and methods described herein can include a pump or other devices for recirculating the fountain solution, as well as devices for recovering the microorganisms present in the fountain solution. Examples of devices for recovering, non-exclusively include apparatuses for filtration, centrifugation, and precipitation (such as cyclones, and the like). In certain embodiments, the pump and/or device for recovery are arranged between the reservoir containing the fountain solution, to be treated and the compartment 2.

[0079] In certain embodiments, the devices and methods provided herein can be connected to a practically any fountain solution distribution, mixing, collection, supply, or circulating system. In more specific embodiments, the devices herein can be connected to the fountain solution systems disclosed in U.S. Patent No. 6,508,069, to Sibilia, U.S. Patent No. 5,713,282 to MacPhee, U.S. Patent No. 5,619,920, to MacPhee, U.S. Patent No. 4,969,480, to Hughes, U.S. Patent No. 4,754,779, to Juhasz, U.S. Patent No. 4,523,854, to Beckley, U.S. Patent No. 4,394,870, to MacPhee et al., and U.S. Patent No. 4,151,854 to Patsko, for example. The above patents are expressly incorporated herein by reference in their entireties.

[0080] New environmental awareness as well as stringent disposal codes have created the need for a system to treat recirculating fountain solution so that it is maintained relatively contaminant free. For example, in many localities the spent fountain solution is classified as hazardous waste. The practice of frequently discarding and replacing the solution has therefore become cost prohibitive. Accordingly, in further embodiments, in addition to treating fountain solution prior to reuse, the methods and devices herein can be used to make the fountain solution suitable for discarding, such as to satisfy governing disposal regulations, for example.

[0081] Typically, fountain solutions primarily comprise water and additional substances. In general, additional substances are added to the fountain solution depending on the specific intended use of the fountain solution. Accordingly, further embodiments include methods of treating fountain solutions containing agents that regulate the pH, ensure compatibility with the printing ink, or keep the printing plate moist. In still further

embodiments, the methods herein can treat fountain solutions containing one or more of the following agents: chelate formers, solvents, preservatives (including biocides), surfactants, corrosion inhibitors (*e.g.*, zinc nitrate, magnesium nitrate, aluminum nitrate), defoamers, dyes, viscosity control agents, emulsion control agents, non-piling agents (*e.g.*, glycols), de-sensitizing salts (*e.g.*, silicates, phosphates), water soluble gums (*e.g.*, gum arabic, larch gum, starches, CMC, PVP, and acrylics), or lubricants (*e.g.*, alcohol, alcohol substitutes, polymers, and glycols), and the like.

[0082] Typical biocides that can be can be used in limited amounts with the methods described herein, include Bromopol [1,3-propanediol, 2-bromo-2-nitro], various isothiazolones, glutaraldehyde, sodium benzoate, phenol, 6-acetoxy-2,4-dimethyl-m-dioxane, 1,2-benziso-thiazolin-3-one, 2-[(hydroxymethyl) amino]ethanol, formaldehyde, quaternary ammonium salt of the trialkyl benzyl type, and the like.

[0083] In more specific embodiments, the methods and devices provided herein can be used to treat fountain solution used in practically any type of offset printing, or printing that is based on water and oil being immiscible. In even more specific embodiments, the methods and devices herein can be used to treat fountain solution used in practically any lithographic printing system.

[0084] Examples of fountain solutions that the methods and devices herein can treat, include, but are not limited to the fountain solutions disclosed in U.S. Patent No. 5,897,693, to Whitehead, U.S. Patent No. 5,720,800, to Matsumoto, U.S. Patent No. 5,695,550 to Marx, et al., U.S. Patent No. 5,637,444, to Matsumoto, U.S. Patent No. 5,308,388, to Schell, U.S. Patent No. 5,279,648 to Chase, U.S. Patent No. 5,164,000 to Gamblin, and U.S. Patent No. 4,854,969, to Bassemir, et al. Each of these patents are hereby expressly incorporated by reference in their entireties.

[0085] In further embodiments, the methods herein can be used in conjunction with one or more other methods that prevent microbial propagation in fountain solutions, including: centrifuging, filtering, aerating, cleaning the sump, maintaining proper concentration of fountain solution, adding biocides, and the like, for example. Accordingly, in certain embodiments, the methods provided herein relate to applying high-frequency ultrasound either before, during, or after one or more the above-mentioned treatment methods, or other like microbial treatments. Examples of apparatuses for treating fountain solutions that the methods herein can be used in conjunction with are disclosed in U.S.

Patent No. 6,293,198, to Mizuno and U.S. Patent No. 5,622,620 to Meenan, et al., for example. Both of these patents are expressly incorporated by reference in their entireties.

[0086] While the foregoing description details certain embodiments of the teachings herein, it will be appreciated, however, that no matter how detailed the foregoing appears in text, the devices and methods herein can be practiced in many ways. As is also stated above, it should be noted that the use of particular terminology when describing certain features or aspects of the teachings herein should not be taken to imply that the terminology is being re-defined herein to be restricted to including any specific characteristics of the features or aspects of the teachings herein with which that terminology is associated. The scope of the teachings herein should therefore be construed in accordance with the appended claims and any equivalents thereof.

WHAT IS CLAIMED IS:

1. A method of treating a cutting fluid comprising simultaneously exposing said cutting fluid to gas microbubbles and ultrasound of a frequency of 200 kHz or higher.

2. The method of Claim 1, wherein said gas microbubbles consist essentially of ambient air.

3. The method of Claim 1, wherein the diameter of said microbubbles is less than about 50 micrometers.

4. An apparatus for reducing the presence of live microorganisms in a cutting fluid comprising:

a compartment for holding a reservoir of cutting fluid;

an ultrasound emitter configured to emit ultrasound signals at a frequency higher than 200 kHz into said compartment; and

a gas microbubble emitter configured to emit gas microbubbles having an average diameter of less than 1 mm into the ultrasound field in the compartment containing the cutting fluid.

5. The apparatus according to Claim 4, wherein the gas microbubbles are not ozone microbubbles.

6. The apparatus according to Claim 4, wherein the gas microbubbles are selected from the group consisting of air and oxygen microbubbles.

7. The apparatus according to Claim 4, wherein the cutting fluid is a water-soluble cutting fluid.

8. The apparatus according to Claim 4, wherein the cutting fluid is a synthetic cutting fluid.

9. The apparatus according to Claim 4, wherein the cutting fluid is a semi-synthetic cutting fluid.

10. The apparatus according to Claim 4, wherein the average diameter of the gas microbubbles is less than 50 μm.

11. The apparatus according to Claim 4, wherein the average diameter of the gas microbubbles is less than 30 μm.

12. The apparatus according to Claim 4, wherein the ultrasound emitted into the compartment does not generate a stationary field phenomenon.

13. The apparatus according to Claim 4, further comprising an electromagnetic radiation emitter configured to emit electromagnetic radiation in the visible range into the ultrasound field.

14. The apparatus according to Claim 4, wherein the microorganisms are bacteria.

15. A method of treating cutting fluid comprising:

collecting cutting fluid from a fluid routing circuit;

routing said cutting fluid into a compartment;

simultaneously exposing said cutting fluid in compartment to gas microbubbles and ultrasound of a frequency of 200 kHz or higher.

16. The method of Claim 15, wherein said gas microbubbles consist essentially of ambient air.

17. The method of Claim 15, wherein the diameter of said microbubbles is less than about 50 micrometers.

18. A machining system comprising:

a cutting device;

a cutting fluid circuit connected to the cutting device;

a compartment for holding a reservoir of cutting fluid through which said cutting fluid is routed;

an ultrasound emitter configured to emit ultrasound signals at a frequency higher than 200 kHz into said compartment; and

a gas microbubble emitter configured to emit gas microbubbles having an average diameter of less than 1 mm into the ultrasound field in the compartment containing the cutting fluid.

19. The apparatus according to 18, wherein the gas microbubbles are not ozone microbubbles.

20. The apparatus according to Claim 18, wherein the gas microbubbles are selected from the group consisting of air and oxygen microbubbles.

21. The apparatus according to Claim 18, wherein the cutting fluid is a water-soluble cutting fluid.

22. The apparatus according to Claim 18, wherein the cutting fluid is a synthetic cutting fluid.

23. The apparatus according to Claim 18, wherein the cutting fluid is a semi-synthetic cutting fluid.

24. The apparatus according to Claim 18, wherein the average diameter of the gas microbubbles is less than 50 μm.

25. The apparatus according to Claim 18, wherein the average diameter of the gas microbubbles is less than 30 μm.

26. The apparatus according to Claim 18, wherein the ultrasound emitted into the compartment does not generate a stationary field phenomenon.

27. The apparatus according to Claim 18, further comprising an electromagnetic radiation emitter configured to emit electromagnetic radiation in the visible range into the ultrasound field.

28. A method of treating a fountain solution comprising simultaneously exposing said fountain solution to gas microbubbles and ultrasound of a frequency of 100 kHz or higher.

29. The method of Claim 28, wherein said gas microbubbles consist essentially of ambient air.

30. The method of Claim 28, wherein the average diameter of the gas microbubbles is less than about 50 μm.

31. An apparatus for reducing the presence of live microorganisms in a fountain solution comprising:

a compartment for holding a reservoir of fountain solution;

an ultrasound emitter configured to emit ultrasound signals at a frequency higher than 100 kHz into said compartment; and

a gas microbubble emitter configured to emit gas microbubbles having an average diameter of less than 1 mm into the ultrasound field in the compartment containing the fountain solution.

32. The apparatus according to Claim 31, wherein the gas microbubbles are not ozone microbubbles.

33. The apparatus according to Claim 31, wherein the gas microbubbles are selected from the group consisting of air and oxygen microbubbles.

34. The apparatus according to Claim 31, wherein the average diameter of the gas microbubbles is less than 50 μm.

35. The apparatus according to Claim 31, wherein the average diameter of the gas microbubbles is less than 30 μm.

36. The apparatus according to Claim 31, wherein the ultrasound emitted into the compartment does not generate a stationary field phenomenon.

37. The apparatus according to Claim 31, further comprising an electromagnetic radiation emitter configured to emit electromagnetic radiation in the visible range into the ultrasound field.

38. The apparatus according to Claim 31, wherein the microorganisms are bacteria.

39. A method of treating fountain solution comprising:

collecting fountain solution from a fluid routing circuit;

routing said fountain solution into a compartment;

simultaneously exposing said fountain solution in compartment to gas microbubbles and ultrasound of a frequency of 100 kHz or higher.

40. The method of Claim 39, wherein said gas microbubbles consist essentially of ambient air.

41. The method of Claim 39, wherein the average diameter of said microbubbles is less than about 50 micrometers.

42. A machining system comprising:

a printing apparatus;

a fountain solution circuit connected to the printing apparatus;

a compartment for holding a reservoir of fountain solution through which said fountain solution is routed;

an ultrasound emitter configured to emit ultrasound signals at a frequency higher than 100 kHz into said compartment; and

a gas microbubble emitter configured to emit gas microbubbles having an average diameter of less than 1 mm into the ultrasound field in the compartment containing the fountain solution.

43. The apparatus according to 42, wherein the gas microbubbles are not ozone microbubbles.

44. The apparatus according to Claim 42, wherein the gas microbubbles are selected from the group consisting of air and oxygen microbubbles.

45. The apparatus according to Claim 42, wherein the average diameter of the gas microbubbles is less than 50 μm.

46. The apparatus according to Claim 42, wherein the average diameter of the gas microbubbles is less than 30 μm.

47. The apparatus according to Claim 42, wherein the ultrasound emitted into the compartment does not generate a stationary field phenomenon.

48. The apparatus according to Claim 42, further comprising an electromagnetic radiation emitter configured to emit electromagnetic radiation in the visible range into the ultrasound field.

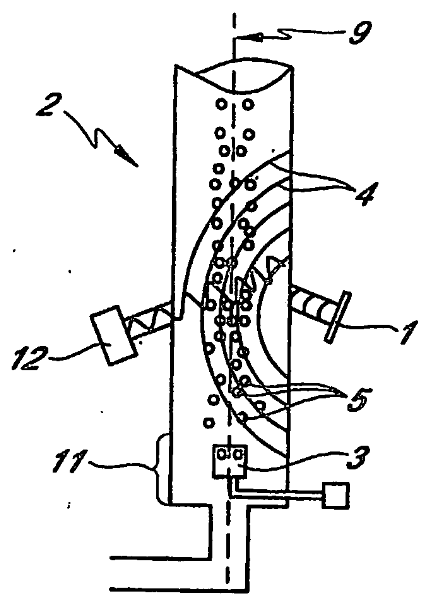

FIG. 1

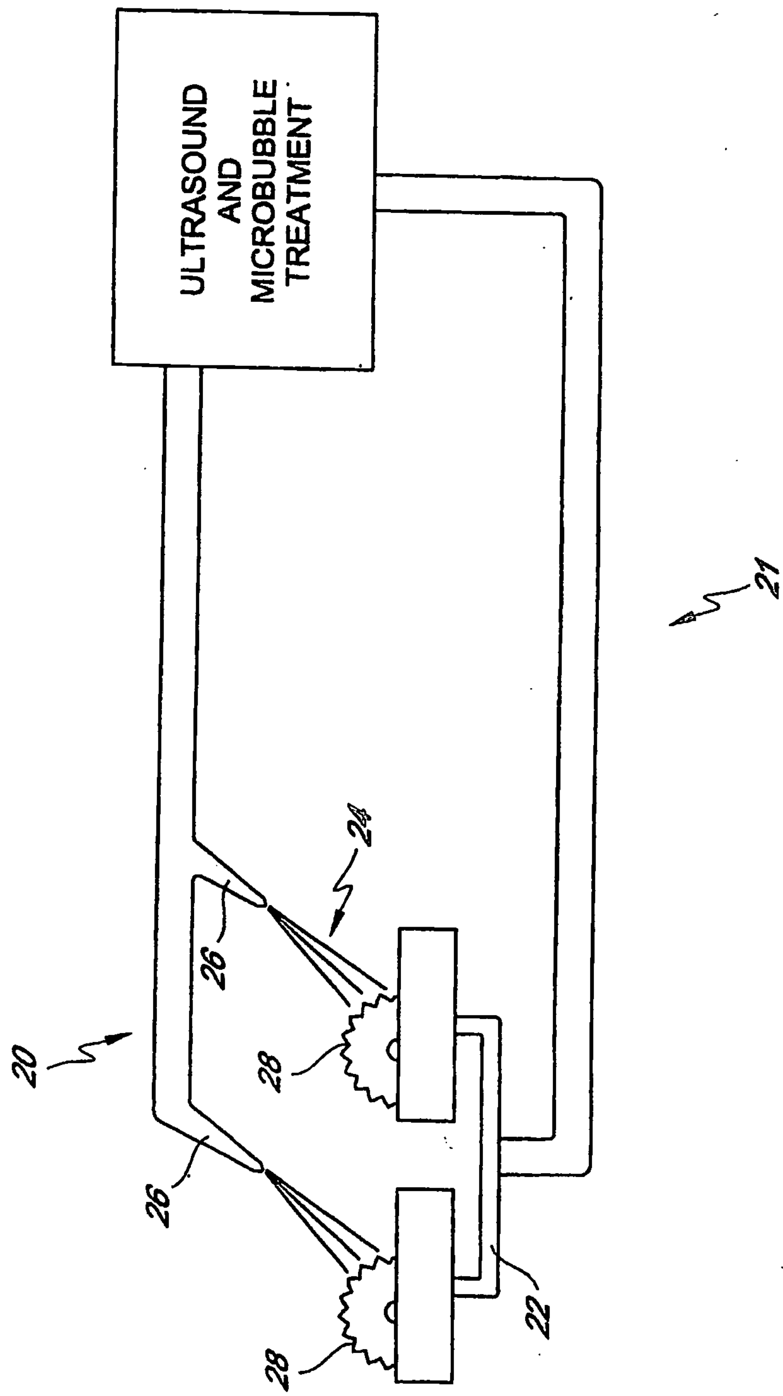

FIG. 2

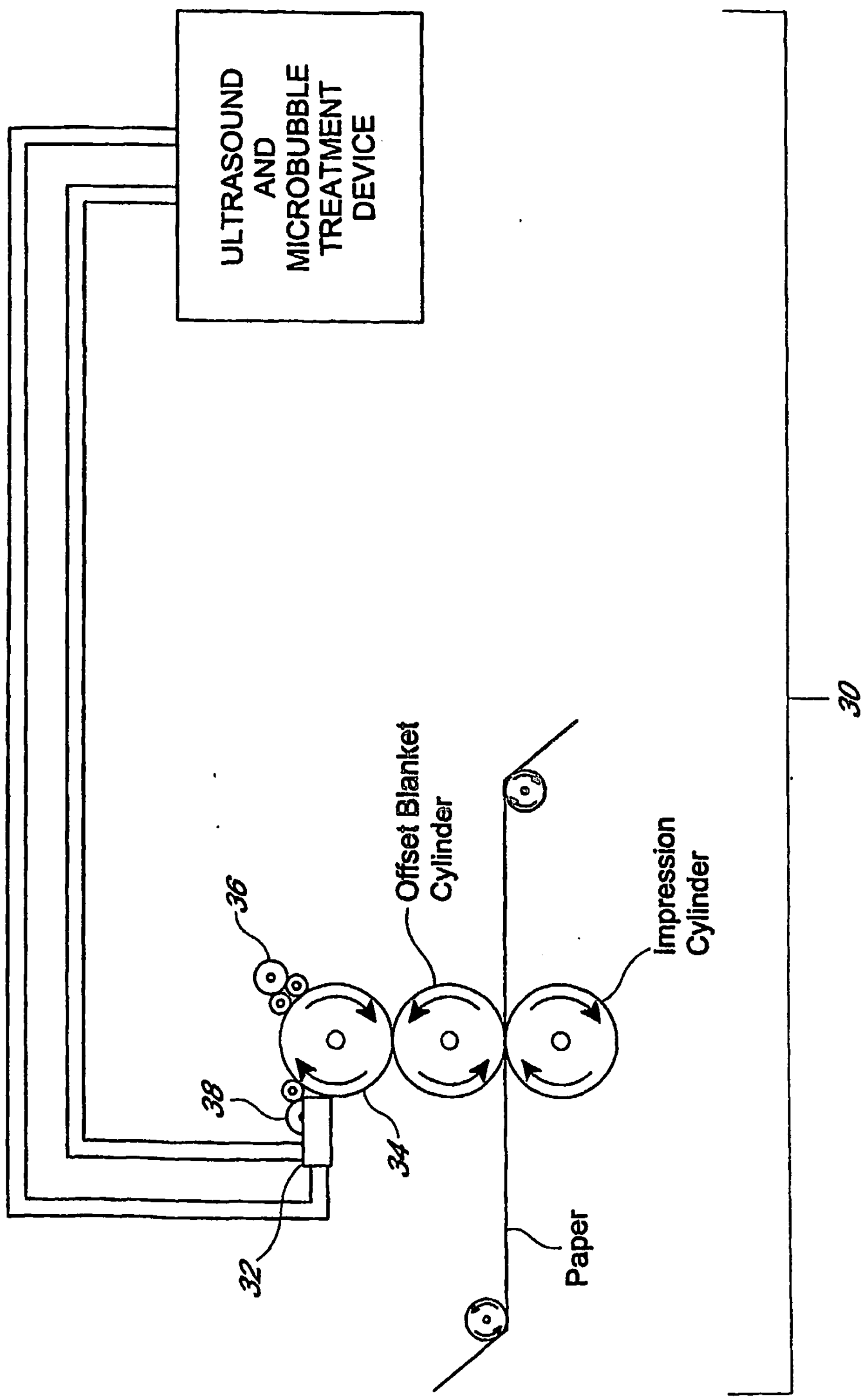
ULTRASOUND
AND
MICROBUBBLE
TREATMENT
DEVICE
Offset Blanket
Cylinder
Impression
Cylinder
Paper
30
32
34
36
38

FIG. 3

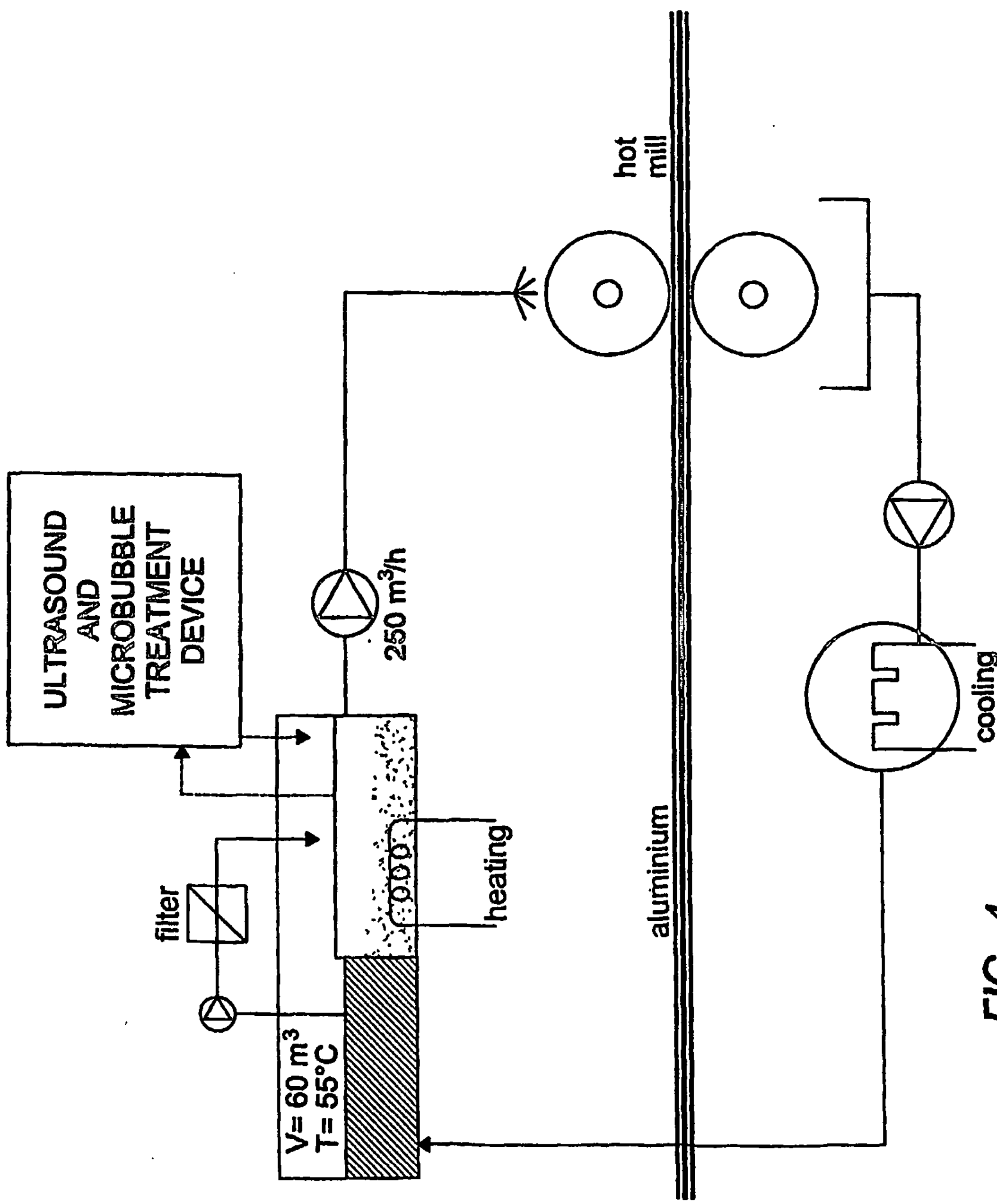
ULTRASOUND AND MICROBUBBLE TREATMENT DEVICE
filter
V= 60 m^3
T= 55°C
heating
250 m^3/h
hot mill
aluminium
cooling

FIG. 4

INTERNATIONAL SEARCH REPORT	International application No. PCT/US04/21664

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C02F 1/36
US CL : 210/748; 422/20, 128
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 210/,542, 748; 422/20, 128

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,T	US 6,770,248 B2 (HAGGETT et al) 03 August 2004, column 3 lines 60-67, column 4 lines 1-4, abstract.	1-48
Y	US 5,380,411 A (SCHLIEF) 10 January 1995, column 1 lines 35-42, column 2 lines 10-16, lines 53-55.	1-48

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 November 2004 (01.11.2004)	10 NOV 2004

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Continuation of B. FIELDS SEARCHED Item 3:
EAST

search terms: fluid, cleaning, treating, ultrasound, microbubbles